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⑤④ **ELECTROLUMINESCENT DEVICES.**

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EP 0 423 283 B1

Descripti nField of the Invention

- 5 The present invention relates to electroluminescent (EL) devices, and in particular EL devices in which the light-emitting layer is a semiconductor.

Background of the Invention

- 10 Electroluminescent (EL) devices are structures which emit light when subject to an applied electric field. The usual model for the physical process in a semiconductor used in this way is through the radiative combination of electron-hole pairs which are injected into the semiconductor from opposite electrodes. Common examples are light-emitting diodes based on GaP and similar III-V semiconductors. Though these devices are efficient and widely used, they are limited in size, and are not easily or economically used in large area displays.
- 15 Alternative materials which can be prepared over large areas are known, and among the inorganic semiconductors most effort has been directed to ZnS. This system has considerable practical drawbacks, primarily poor reliability. The mechanism in ZnS is believed to be one where acceleration of one type of carrier through the semiconductor under a strong electric field causes local excitation of the semiconductor which relaxes through radiative emission.

- 20 Among organic materials, simple aromatic molecules such as anthracene, perylene and coronene are known to show electroluminescence. The practical difficulty with these materials is, as with ZnS, their poor reliability, together with difficulties in deposition of the organic layers and the current-injecting electrode layers. Techniques such as sublimation of the organic material suffer from the disadvantage that the resultant layer is soft, prone to recrystallisation, and unable to support high temperature deposition of top-contact layers.
- 25 Techniques such as Langmuir-Blodgett film deposition of suitably-modified aromatics suffer from poor film quality, dilution of the active material, and high cost of fabrication.

- An electroluminescent device utilising anthracene is disclosed in US-A-3,621,321. This device suffers from high power consumption and low luminescence. In an attempt to provide an improved device, US-A-4,672,265 describes an EL device having a double layer structure as its luminescent layer. However, the suggested materials for the double layer structure are organic materials which suffer from the disadvantages mentioned above.
- 30

Reference is also made to an article in the Japanese Journal of Applied Physics, Vol. 21, No. 6, June 1982, pages 860-864 entitled "Electroluminescence in Polyethylene Terephthalate (PET) I. Impulse voltage". This describes an electroluminescent device made with the polymer PET.

- 35 The present invention provides in one aspect an electroluminescent device comprising: a light emissive layer in the form of a thin dense polymer film comprising at least one polymer; a first contact layer arranged on one side of the light emissive layer selected so that on application of an electric field to said device charge carriers of a first type are injected into the light emissive layer; and a second contact layer arranged on the other side of the light emissive layer characterised in that the second contact layer is selected so that on application of an electric field to said device charge carriers of a second type are injected into the light emissive layer; and the light emissive layer comprises a semiconductive conjugated polymer layer present in a volume fraction which allows the percolation threshold for charge transport to be achieved, said semiconductive conjugated polymer having a sufficiently low concentration of extrinsic charge carriers that on applying an electric field between the first and second contact layers across the light emissive layer so as to render the second
- 40 contact layer positive relative to the first contact layer charge carriers of said first and second types are injected into the light emissive layer and combine to form charge carrier pairs in the semiconductive conjugated polymer which pairs decay radiatively so that radiation is emitted from said conjugated polymer.
- 45

The invention is based on the discovery by the present inventors that semiconductive conjugated polymers can be caused to exhibit electroluminescence by the injection of charge carriers from suitable contact layers.

- 50 Semiconductive conjugated polymers per se are known. For example, their use in an optical modulator is discussed in EP-A-0294061. In that case, polyacetylene is used as the active layer in a modulating structure between first and second electrodes. It is necessary to place an insulating layer between one of the electrodes and the active layer so as to create a space charge region in the active layer which gives rise to the optical modulation effect. Such a structure could not exhibit electroluminescence since the presence of the space charge layer precludes the formation of electron/hole pairs whose decay gives rise to radiation. It will be clear in any event that the exhibition of electroluminescence in EP-A-0294061 would be wholly undesirable since the optical modulation effect would be disrupted thereby.
- 55

In the device of the present invention, the conjugated polymer is preferably poly (p-phenyl nevinyl ne)

[PPV] and the first charge injecting contact layer is a thin layer of aluminium on a surface having formed a thin oxide layer, the first surface of the semiconducting layer being in contact with the said oxide layer and the second charge injecting contact layer is a thin layer of aluminium or gold.

In another embodiment, the conjugated polymer is PPV, the first contact layer is aluminium or an alloy of magnesium and silver and the second contact layer is indium oxide.

In yet another embodiment, the conjugated polymer is PPV and one of the contact layers is non-crystalline silicon and the other of the contact layers is selected from the group consisting of aluminium, gold, magnesium/silver alloy and indium oxide.

These embodiments can be made by putting down either the first contact layer or the second contact layer onto a substrate, applying a thin film of PPV and then putting down the other of the first and second contact layers.

Preferably the polymer film is of substantially uniform thickness in the range 10 nm to 5 μ m and the conjugated polymer has a semiconductor band gap in the range 1eV to 3.5eV. Furthermore the proportion of the conjugated polymer in the electroluminescent areas of the polymer film is sufficient to achieve the percolation threshold for charge transport in the conjugated polymer present in the film.

A second aspect of the present invention provides a method of manufacture of an electroluminescent device comprising providing a layer of a light emissive polymer between first and second contact layers, wherein the first contact layer is selected so that an application of an electric field to said device charge carriers of a first type are injected into the light emissive layer, characterised by the steps of: a) putting down one of said first and second contact layers; b) depositing on said contact layer a layer of a precursor polymer as a polymer film and then heating the deposited precursor polymer to a high temperature to form the light emissive layer as a semiconductive conjugated polymer; and c) providing the other one of said first and second contact layers, the second contact layer being selected and arranged so that on application of an electric field to said device charge carriers of a second type are injected into the light emissive layer, wherein the semiconductive conjugated polymer has a sufficiently low concentration of extrinsic charge carriers that on applying an electric field between the first and second contact layers across a semiconductor layer so as to render the second contact layer positive relative to the first contact layer charge carriers of said first and second types are injected into the semiconductor layer and combine to form in the conjugated polymer charge carrier pairs which decay radiatively so that radiation is emitted from the conjugated polymer.

By conjugated polymer is meant a polymer which possesses a delocalised π -electron system along the polymer backbone; the delocalised π -electron system confers semiconducting properties to the polymer and gives it the ability to support positive and negative charge carriers with high mobilities along the polymer chain. Such polymers are discussed for example by R.H. Friend in Journal of Molecular Electronics 4 (1988) January-March, No. 1, pages 37 to 46.

It is believed that the mechanism underlying the present invention is such that the positive contact layer injects positive charge carriers into the polymer film and the negative contact layer injects negative charge carriers into the polymer film, these charge carriers combining to form charge carrier pairs which decay radiatively. To achieve this, preferably the positive contact layer is selected to have a high work function and the negative contact layer to have a low work function. Hence the negative contact layer comprises an electron-injecting material, for example a metal or a doped semiconductor that, when placed in contact with the polymer semiconductor layer and made negative with respect to the polymer semiconductor through application of an external potential across the circuit, allows the injection of electrons into the polymer semiconductor layer. The positive contact layer comprises a hole-injecting material, for example a metal or a doped semiconductor that, when placed in contact with the polymer semiconductor layer and made positive with respect to the polymer semiconductor through application of an external potential across the circuit, allows the injection of positive charges, commonly termed "holes", into the polymer semiconductor layer.

In order to produce the desired electroluminescence, the polymer film must be substantially free of defects which act as non-radiative recombination centres, since such defects prevent electroluminescence.

By "dense" polymer film is meant that the polymer film is not fibrillar and is substantially free of voids.

One or each of the contact layers can include, in addition to the layer of charge injecting material, a further layer of a material, preferably an organic material, which serves to control the injection ratio of electrons and holes into the EL layer and to ensure that radiative decay takes place away from the charge injecting material of the contact layers.

The film of conjugated polymer preferably comprises a single conjugated polymer or a single co-polymer which contains segments of conjugated polymer. Alternatively, the film of conjugated polymer may consist of a blend of a conjugated polymer or copolymer with another suitable polymer.

Further preferred features of the polymer film are that:

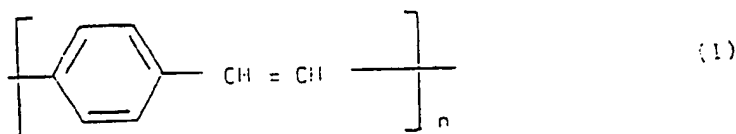
(i) the polymer should be stable to oxygen, moisture, and to exposure to elevated temperatures;

(ii) the polymer film should have good adhesion to an underlying layer, good resistance to thermally-induced and stress-induced cracking, and good resistance to shrinkage, swelling, or crystallisation or other morphological changes;

(iii) the polymer film should be resilient to ion/atomic migration processes, e.g. by virtue of a high crystallinity and high melting temperature.

Embodiments of the present invention will now be described by way of example only, with reference to the accompanying drawings.

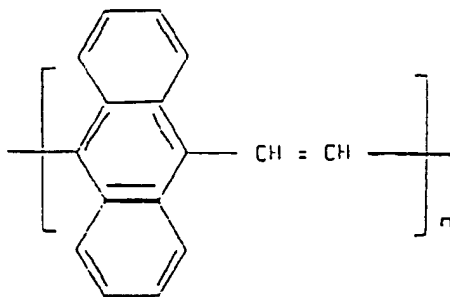
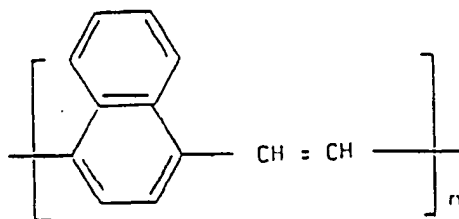
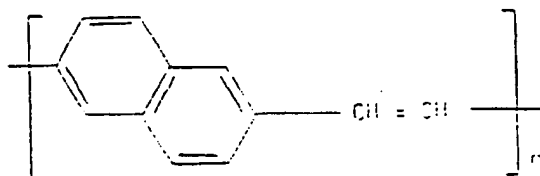
The film of conjugated polymer is preferably a film of a poly(p-phenylenevinylene) [PPV] of formula



wherein the phenylene ring may optionally carry one or more substituents each independently selected from alkyl (preferably methyl), alkoxy (preferably methoxy or ethoxy), halogen (preferably chlorine or bromine), or nitro.

Other conjugated polymers derived from poly(p-phenylenevinylene) are also suitable for use as the polymer film in the EL devices of the present invention. Typical examples of such derivatives are polymers derived by:

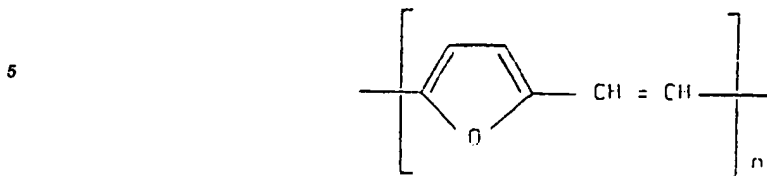
(i) replacing the phenylene ring in formula (1) with a fused ring system, eg replacing the phenylene ring with an anthracene or naphthalene ring system to give structures such as:-



These alternative ring systems may also carry one or more substituents of the type described above in relation to the phenylene ring.

(ii) replacing the phenylene ring with a heterocyclic ring system such as a furan ring to give structures such

as:-

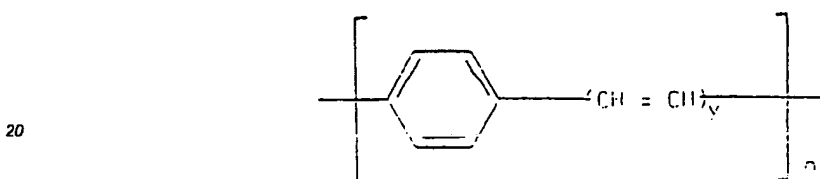


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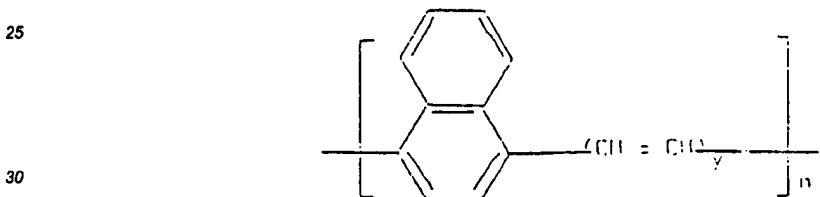
As before, the furan ring may carry one or more substituents of the type described above in relation to phenylene rings.

(iii) increasing the number of vinylene moieties associated with each phenylene ring (or each of the other alternative ring systems described above in (i) and (ii)) to give structures such as:-

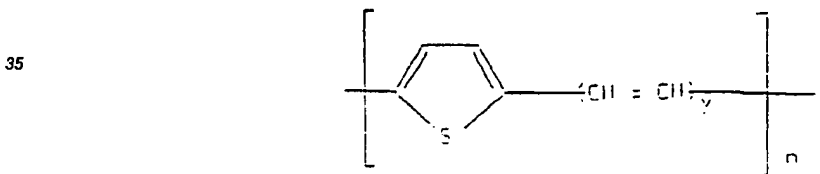
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wherein y represents 2, 3, 4, 5, 6, 7,

Once again, the ring systems may carry the various substituents described above.

These various different PPV derivatives will possess different semiconductor energy gaps; this should permit the construction of electroluminescent devices which have emission at different wavelengths covering the entire visible part of the spectrum.

The film of conjugated polymer may be prepared by means of a chemical and/or thermal treatment of a solution - processible or melt-processible "precursor" polymer. The latter can be purified or pre-processed into the desired form before subsequent transformation to the conjugated polymer via an elimination reaction.

Films of the various derivatives of PPV described above can be applied onto a conducting substrate in similar manner by using an appropriate sulphonium precursor.

In certain circumstances it may be advantageous to use polymer precursors which have a higher solubility in organic solvents than the sulphonium salt precursors (II). Enhanced solubility in organic solvents can be achieved by replacing the sulphonium moiety in the precursor by a less hydrophilic group such as an alkoxy group (usually methoxy), or a pyridinium group.

Typically, a film of poly(phenylenevinylene) is applied onto a conducting substrate by a method which relies on a reaction scheme such as is illustrated in Figure 1. The sulphonium salt monomer (II) is converted into a precursor polymer (III) in aqueous solution or in a solution of methanol/water, or methanol. Such a solution of the precursor-polymer (III) can be applied onto a conducting substrate by means of standard spin-coating tech-

niques as used in the semiconductor industry for photoresist processing. The resultant film of precursor-polymer III can then be converted into poly(phenylene vinylene) (I) by heating to temperatures typically in the range 200-350°C.

Details of the conditions necessary for the chemical synthesis of the monomer (II), its polymerisation to the precursor (III) and its thermal conversion to PPV are described in the literature, for example in D.D.C. Bradley, J. Phys. D (Applied Physics) 20, 1389 (1987); and J.D. Stenger Smith, R.W. Lenz and G. Wegner, Polymer 30, 1048 (1989).

We have found that with poly(phenylenevinylene) films of a thickness in the range 10 nm to 10 micrometres can be obtained. These PPV films are found to have very few pin holes. The PPV film has a semiconductor energy gap of about 2.5eV (500nm); it is robust, shows little reaction with oxygen at room temperature, and is stable out of air at temperatures well in excess of 300°C.

Enhanced ordering in the conjugated material may be achieved by modifying the leaving group of the precursor polymer to ensure that the elimination proceeds smoothly via a simple reaction without generation of additional intermediate structures. Thus, for example, the normal dialkyl sulphonium moiety can be replaced with a tetrahydrothiophenium moiety. The latter eliminates as a single leaving group without decomposition, as is seen for dialkyl sulphide, into an alkyl mercaptan. In the examples described here, the precursor polymers used include both that with dimethyl sulphide and tetrahydrothiophene as the leaving group. Both precursors produce film of PPV suitable for use in the device structures shown in examples below.

A further material which may be suitable for forming the film of conjugated polymer is poly(phenylene). This material may be prepared by starting from biologically synthesised derivatives of 5,6-dihydroxycyclohexa-1,3-dienes. These derivatives can be polymerised by use of radical initiators into a polymer precursor that is soluble in simple organic solvents. This preparation of poly(phenylene) is more fully described in Ballard et al, J. Chem. Soc. Chem. Comm. 954 (1983).

A solution of the polymer precursor can be spin coated as a thin film onto a conducting substrate and then be converted to the conjugated poly(phenylene) polymer by a heat treatment, typically in the range 140 to 240°C.

Copolymerisation with vinyl or diene monomers can also be performed so as to obtain phenylene copolymers.

A further category of materials which can be used to form the required film of conjugated polymer is a conjugated polymer which is itself either solution processible or melt processible by virtue of the presence of bulky pendant side groups attached to the main conjugated chain or by virtue of the inclusion of the conjugated polymer into a copolymer structure of which one or more components are non-conjugated. Examples of the former include:-

(a) Poly(4,4'-diphenylenediphenylvinylene) [PDPV] is an arylene vinylene polymer in which both vinylene carbons are substituted by phenyl rings. It is soluble in common organic solvents thus enabling the preparation of thin films.

(b) Poly(1,4-phenylene-1-phenylvinylene) and poly(1,4-phenylenediphenylvinylene) polymers are analogues of PPV in which respectively one and both vinylene carbons are substituted with phenyl groups. They are both soluble in organic solvents and may be cast or spun into thin film form.

(c) Poly(3-alkylthiophene) polymers (alkyl is one of propyl, butyl, pentyl, hexyl, heptyl, octyl, decyl, undecyl, dodecyl etc) which are solution processible in common organic solvents and which for longer alkyl sequences (alkyl greater than or equal to octyl) are also melt processible.

(d) Poly(3-alkylpyrrole) polymers which are expected to be similar to the poly(3-alkylthiophene) polymers.

(e) Poly(2,5-dialkoxy-p-phenylenevinylene) polymers with alkyl greater than butyl are solution processible.

(f) Poly(phenylacetylene) is a derivative of polyacetylene in which the hydrogen atoms along the chain are replaced by phenyl groups. This substitution renders the material soluble.

In some circumstances it may also be appropriate to form polymer blends of the conjugated polymer with other polymers so as to obtain the required processibility of the polymer and thereby facilitate forming of the required thin uniform films of the polymer on the conducting substrate (the charge injecting contact layer).

When such copolymers or polymer blends are used to form the film of conjugated polymer, the active region of the electroluminescent device which incorporates the said film of conjugated polymer must contain a volume fraction of conjugated polymer which is greater than or equal to the percolation threshold of the copolymer or polymer blend.

The semiconductor electroluminescent layer may be formed as a composite layer with layers of polymers with different band gaps and/or majority charge species so that, for example, concentration of the injected charge, from the charge injecting contact layer, within a particular region of the EL device may be achieved. Composite layers may be fabricated by successive deposition of polymer layers. In the case where films are deposited in the form of the precursor by spin- or draw-coating to the conjugated polymer, the conversion proc-

ess to the conjugated polymer renders the film insoluble, so that subsequent layers may be similarly applied without dissolution of the previously deposited film.

Brief description of the drawings

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For a better understanding of the present invention, and to show how the same may be carried into effect, reference will now be made, by way of example, to the accompanying drawings in which:

- Figure 1 is a formulae drawing showing a reaction scheme for laying down the conjugated polymer;
 Figures 2 and 3 are sketches of an electroluminescent device in accordance with the present invention;
 10 Figure 4 is a graph of the electroluminescent output of the device described with reference to Figures 2 and 3;
 Figures 5 and 6 are graphs of current flow VS light emission, and output intensity VS applied voltage, respectively for an electroluminescent device according to another example of the invention; and
 15 Figures 7 and 8 are graphs respectively of the current output and electroluminescent intensity of a further example of the invention.

Description of the preferred embodiments

Example 1

20

Referring now to Figures 2 and 3 an EL device was constructed as follows:

Onto the upper surface of a substrate of glass for example a silica or borosilicate glass 1 of approximately 1mm thickness, a first charge injecting contact layer 2 was formed. The charge injecting contact layer was formed by thermal evaporation of aluminium through a shadow-mask resulting in a layer of approximately 20
 25 nm in thickness. The shadow-mask was used to define a pattern which was a series of parallel strips of width 2mm, separation 2mm and length 15 mm. The resulting aluminium charge injecting contact layer was then exposed to the air to allow formation of a thin surface oxide layer 3. This then formed the electron injecting contact layer.

A solution of the precursor to PPV, in methanol, having a concentration in the range 1 gram polymer to 10 to 25 ml of methanol, was spin-coated onto the combination substrate described above. This was achieved by spreading the polymer solution over the whole surface of the combination substrate and then spinning the substrate, held with its upper surface horizontal, about a vertical axis at speeds of up to 5000 r.p.m. The resultant substrate and precursor polymer layer was then heated in a vacuum oven at a temperature of 300°C for 12
 30 hours. This heat treatment converted the precursor polymer to PPV, and the resultant PPV film 4 had a thickness in the range 100 to 300 nm. The minimum requirements for the film thickness is set by the film conductance and a lower limit is in the region of 20 nm. However, the preferred range of thickness is 20 nm to 1 µm.

A second charge injecting contact layer (5) was then formed by the evaporation of gold or aluminium onto the PPV film. A shadow mask was again used to define a pattern on the surface of the PPV film so that a series of parallel strips of width 2mm, separation 2mm and length 15 mm was formed rotated at right angles
 40 to the first charge injecting contact layer strips. The thickness of the second charge injecting contact layer was in the range 20-30nm. This then formed the hole-injecting contact layer.

It is preferable that at least one of the charge injecting contact layers is transparent or semitransparent in order to allow light emission from the EL device perpendicular to the plane of the device. This is achieved here with aluminium and gold layers of a thickness not exceeding 30 nm. For a device with the thickness of the
 45 PPV layer about 200 nm, the threshold voltage for charge injection and the appearance of strong electroluminescence is about 40 volts. The voltage gives a threshold electric field of $2 \times 10^6 \text{ Vcm}^{-1}$. At a current density of 2mA/cm^2 the light emission through the semitransparent electrodes was visible by eye under normal lighting conditions. The output of the device showed only weak dependance on frequencies up to 100 kHz. This demonstrates that the response time of the EL device is very short and is faster than 10 microseconds. When in
 50 use the EL device was operated in air with no special precautions taken and exhibited no obvious indications of degradation.

The light output from the device was spectrally resolved with a grating monochromator and detected with a silicon photovoltaic cell, and measurements were performed both at room temperature (20°C) and also with the device held in a cryostat with optical access, at low temperatures. Results are shown in Figure 4. The EL
 55 spectrum shows light output over the spectral range 690 to 500 nm (1.8 to 2.4 eV) with peaks separated by about 0.15 eV which shift in position a little with temperature.

Other materials which are suitable for use as an electron-injecting contact layer because they have a low work function relative to the EL layer are: n-doped silicon (amorphous or crystalline), silicon with an oxide coat-

ing, alkali and alkaline-earth metals either pure or alloyed with other metals such as Ag. Also thin layers of "n-type doped" conjugated polymers may be interposed between a metallic layer and the electroluminescent polymer layer to form the electron-injecting contact layer.

Other materials which are suitable for use as a hole-injecting contact layer because they have a high work function relative to the EL layer are: indium/tin oxides (which are transparent in the visible part of the spectrum), platinum, nickel, palladium and graphite. Also thin layers of "p-type doped" conjugated polymers, such as electrochemically polymerised polypyrrole or polythiophene may be interposed between a metallic layer and the electroluminescent polymer layer to form the hole-injecting contact layer.

The above mentioned materials may be applied as follows: all metals except those with very high melting point temperatures such as platinum may be deposited by evaporation; all metals including indium/tin oxide may be deposited using DC or RF sputtering and also electron beam evaporation; for amorphous silicon deposition may be done by glow-discharge deposition from mixtures of silane and dopants such as phosphine.

The following are some examples of structures using these materials.

15 Example 2

The structure for this example is built up as a series of layers on a glass substrate. First, a layer of conducting but transparent indium oxide was deposited onto the substrate by a process involving ion-beam sputtering from an indium target in the presence of oxygen.

20 Samples are prepared in cryopumped system with a base pressure of 10^{-6} mbar ($1 \text{ bar} = 10^5 \text{ Pa}$). The substrate is water-cooled, remaining at room temperature for all depositions used here. Ion-beam sputtering from an indium target at deposition rates of typically 0.1 nm/sec , in the presence of an oxygen pressure of typically 2×10^{-4} mbar, produced films of transparent indium oxide with resistivities of typically $5 \times 10^{-4} \Omega \text{ cm}$. Typical thicknesses of 100 nm give specific sheet resistances of about 50Ω per square. Such films have optical transmission coefficients in the visible portion of the spectrum of better than 90%.

These films have an amorphous structure, as determined from X-ray and electron diffraction measurements.

A layer of PPV is next deposited onto the indium oxide layer, using the procedure described in example 1 above. A top contact of aluminium is finally deposited by evaporation, typically to a thickness of 50 nm . This structure is operated with the indium oxide contact layer functioning as the positive contact, and the aluminium contact as the negative contact. Light emission is viewed through the indium oxide layer.

Results for a structure constructed this way, with a layer of PPV of thickness 70 nm , and an active area of 2 mm^2 are shown in Figures 5 and 6. The threshold for current flow associated with light emission is seen to be at about 14 V in Figure 5. The variation in the intensity of the spectrally-integrated light output for the device is shown as a function of current in Figure 6.

Example 3

40 The fabrication of this structure is as for Example 2 above up to the top metal contact. Here, we deposit by evaporation an alloy of silver and magnesium to form the top contact which acts as the negative contact. The evaporation is performed by heating a mixture of silver and magnesium powders in a molar ratio of 1 to 10 in a boat, and film thicknesses of typically 50 nm were deposited.

Magnesium is desirable as a material for the negative electrode as it has a low work function. The addition of silver to form an alloy improves the adhesion of the metal film to the polymer layer, and improves its resistance to oxidation. The current/voltage and EL properties of these samples were similar to those described in Example 2.

Example 4

50 These structures were fabricated with a layer of amorphous silicon-hydrogen alloy acting as the negative electrode, and indium oxide as the positive electrode. A glass substrate is used with an evaporated Metal contact layer of aluminium or chromium. The amorphous silicon-hydrogen film was then deposited by radio-frequency, RF, sputtering as detailed below.

The RF sputter used has two targets, a liquid Nitrogen cooled target and is operated with a target-substrate separation of 8 cm . The chamber has a base pressure of 5×10^{-8} mbar. Magnetron targets are loaded with layers of n-doped Si wafers to a thickness of 3 mm . The targets are cleaned by presputtering for 1-2 hours prior to sample deposition. Substrates prepared as above are radiatively heated so that the temperature at the back side of the 3 cm thick Cu and Al substrate plate is at $250\text{-}300^\circ\text{C}$. Substrates are rotated at about 6

rate is 100 s/min. The sputtering gas used is 30% H₂ in Ar, at a pressure of 0.007-0.013 mbar, and is continually passed through the chamber during deposition. The RF power used is 250W with a reflected power of 2W. Deposition rates are typically 12nm/min giving deposition times of 1.5 hours for film thicknesses of 1 µm.

The resulting amorphous Si is reddish brown in colour and has a d.c. resistivity of between 5×10^6 and $5 \times 10^8 \Omega\text{cm}$. [This found by evaporating two Al pads, either above or below the sample, of length 3 mm and with a separation of 0.25 mm and measuring the resistance between these two contacts].

A layer of PPV was then applied to the amorphous silicon-hydrogen layer, as described in Example 1 above, and this was followed with a layer of indium oxide, deposited directly onto the PPV layer, using the procedure described in Example 2.

Results obtained for a structure fabricated using the steps outlined above are shown in Figures 7 and 8 for a structure of area 14 mm², and layer thicknesses of 1 µm for the silicon-hydrogen, 40 nm for the PPV and 250 nm for the indium oxide. Figure 7 shows the current versus voltage characteristic for the device in forward bias (indium oxide positive), and Figure 8 shows the variation in integrated light output with current. The onset of charge injection and light emission is at about 17 V, and the rise in current above this threshold is, due to the presence here of the resistive silicon-hydrogen layer, more gradual than observed in structures without it, as seen for example in Figure 5.

Structures of this type did also show weaker EL in reverse bias (indium oxide contact negative with respect to the silicon-hydrogen contact). The preferred mode of operation, however, is in forward bias.

20 Example 5

Fabrication as in example 4, but with the top layer of indium oxide replaced by a layer of semitransparent gold or aluminium. Structures fabricated with the top layer of thickness about 20 nm showed EL through this top contact. These devices showed similar characteristics to the examples discussed above.

The method of fabrication of Example 4 could also be used with the contact layers described in Examples 2 and 3.

There are other methods, known per se, for depositing silicon/hydrogen layers and indium oxide layers. For silicon this could include glow discharge of silane and evaporation. For indium oxide other possibilities include tin with the indium, to form indium tin oxide (ITO), which has very similar electrical properties to the indium oxide that we have used here. Deposition methods include evaporation, RF and DC sputtering.

The choice of thickness for the charge injecting contact layers will be determined by the deposition technique used and also the desired optical transparency of the contact layer. The ease of charge injection may be improved by constructing the charge injecting contact layers as composites. Such composites would incorporate thin layers of oxidised and reduced conjugated polymers for hole and electron injection respectively. These extra layers of conjugated polymer may or may not be the same as the active electroluminescent polymer layer. Methods of doping such materials are well known in the field and are clearly described in "Handbook of Conducting Polymers" T.J. Skotheim.

Although in certain circumstances it is preferable that at least one of the charge injecting contact layers is transparent or semitransparent in order to allow emission of radiation perpendicular to the plane of the device it is not necessarily the case for example when emission within the plane of the device only is required.

The limit to the size of the EL device produced is determined by the size of the substrate which can be used for spin-coating. For example, 15 cm diameter silicon wafers have been coated in this way. To coat much larger areas, techniques such as draw-coating may be used instead. It is therefore feasible that EL devices using conjugated polymers with areas of square metres may be constructed.

At least some of the conjugated polymers, including PPV, are capable of withstanding post-processing such as the deposition of metal layers in which the deposition is required to be at very high temperatures for evaporation, or the deposition of amorphous silicon layers, followed by photolithographic processes for the definition of active electroluminescent areas. Although it is preferable, with the use of PPV, for either spin- or draw-coating to be used as the methods for applying the precursor polymer to the substrate depending upon the conjugated polymer and the type of EL device required spin-, draw-coating and melt-processing are all methods which may be used to deposit the conjugated polymer onto the substrate.

The EL device may be used in a variety of ways where electroluminescence is of use. It may be used where semiconductor LED's have traditionally been used. It may also be used where traditionally liquid crystals have been used, the EL device having many properties which make it a desirable alternative to liquid crystals.

Since the EL device is light-emitting in contrast to liquid crystal displays, the viewing angle is wide. Furthermore, large area EL devices can be achieved where problems associated with substrate flatness and spacing have been encountered with large area liquid crystal displays. The EL devices are particularly suitable for matrix-addressed displays for example televisions and computer displays. An example of electroluminescent

devices for use in a matrix-addressed displays is shown in Figure 3 where the charge injecting contact layers are applied in strips, either side of the semiconductor layer, the strips of one contact layer being orthogonal to the strips of the other contact layer. The matrix-addressing of individual EL devices or areas of the semiconductor layer called pixels of the display is achieved by the selection of a particular strip in the lower charge injecting contact layer and a particular strip, at right angles to the first strip, in the upper charge injecting contact layer. Furthermore since the EL device has such a high speed of response then the EL device is suitable for use as a television screen, particularly since the colour of the emitted light may be controlled through the choice of the conjugated polymer and so its semiconductor band gap and so colour displays using green, red and blue pixels, suitable for colour mixing, are possible through the location of different conjugated polymers in the EL device.

Industrial application

EL devices may also be used as individual shaped elements for indicators in vehicle dashboards, on cookers or video recorders for example. Each element may be produced in the required shape for the intended application. Furthermore the EL device need not be flat and could, for example, be formed after fabrication, to follow contours in three dimensions for example the contours of a windscreen in a vehicle or aircraft. For such use the precursor polymer would have to be applied to a suitable substrate such as transparent polymer film such as polyester, polyvinylidene fluoride or polyimide. If the precursor polymer is applied to such flexible polymer films then continuous fabrication of the EL device, onto a roll, is possible. Alternatively the precursor polymer may be applied, using for example a draw-coating process, onto a pre-fabricated contoured substrate.

Finally use of the EL devices is envisaged in optical communications where the EL device may be fabricated directly onto a prepared structure to act as a light source with efficient optical coupling of the EL device with optical fibres and/or thin-film waveguides. A similar application is described in an article by Satoshi Ishihara in Science and Technology in Japan of July 1989, pages 8 to 14 entitled "Optical Information Processing".

EL device light sources may be suitable for use as lasers.

Claims

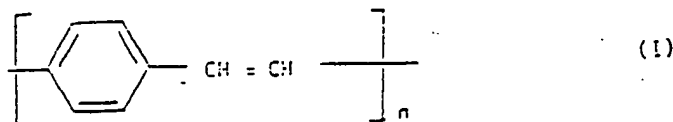
1. An electroluminescent device comprising:

a light emissive layer (4) in the form of a thin dense polymer film comprising at least one polymer;
a first contact layer (2) arranged on one side of the light emissive layer selected so that on application of an electric field to said device charge carriers of a first type are injected into the light emissive layer; and

a second contact layer (5) arranged on the other side of the light emissive layer characterised in that the second contact layer is selected so that on application of an electric field to said device charge carriers of a second type are injected into the light emissive layer; and

the light emissive layer comprising a semiconductive conjugated polymer present in a volume fraction which allows the percolation threshold for charge transport of the polymer film to be achieved, said semiconductive conjugated polymer having a sufficiently low concentration of extrinsic charge carriers that on applying an electric field between the first and second contact layers across the light emissive layer so as to render the second contact layer positive relative to the first contact layer charge carriers of said first and second types are injected into the light emissive layer and combine to form charge carrier pairs in the semiconductive conjugated polymer which pairs decay radiatively so that radiation is emitted from said conjugated polymer.

2. An electroluminescent device as claimed in claim 1, wherein the conjugated polymer is poly(p-phenylenevinylene) [PPV] of formula



wherein the phenylene ring may optionally carry one or more substituents each independently selected

from alkyl (preferably methyl), alkoxy (preferably methoxy or ethoxy), halogen (preferably chlorine or bromine), or nitro.

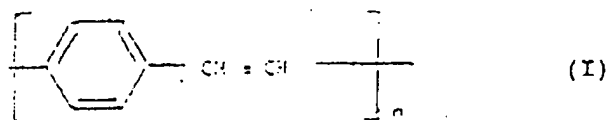
3. An electroluminescent device as claimed in either of claims 1 or 2, wherein the thin dense polymer film is of substantially uniform thickness in the range 10nm to 5µm.
4. An electroluminescent device as claimed in any of the preceding claims, wherein the conjugated polymer has a semiconductor band gap in the range 1eV to 3.5eV.
5. An electroluminescent device as claimed in any of the preceding claims, wherein the first charge injecting contact layer is a thin layer of aluminium (2) one surface having formed a thin oxide layer (3), the first surface of the semiconductor layer (4) being in contact with the said oxide layer.
6. An electroluminescent device as claimed in any of claims 1 to 4 wherein the first contact layer is selected from the group comprising aluminium or an alloy of magnesium and silver.
7. An electroluminescent device as claimed in claim 5, wherein the second charge injecting contact layer (5) is selected from the group comprising aluminium and gold.
8. An electroluminescent device as claimed in any of the preceding claims, wherein at least one of the first and second charge injecting contact layers is at least semi-transparent.
9. An electroluminescent device as claimed in claim 6, wherein the second contact layer (5) comprises indium oxide or indium tin oxide.
10. An electroluminescent device as claimed in any of claims 1 to 4, wherein the first contact layer comprises amorphous silicon and the second contact layer is selected from the group comprising aluminium, gold and indium oxide.
11. An electroluminescent device as claimed in any of the preceding claims, wherein at least one of the first and second charge injecting contact layers is also in contact with a supporting substrate.
12. An electroluminescent device as claimed in claim 11, wherein the supporting substrate is silica glass.
13. An electroluminescent device as claimed in claim 11 or 12 wherein the supporting substrate is a flexible transparent polymer.
14. An array of electroluminescent devices, each electroluminescent device as claimed in any of the preceding claims, said first and second charge injecting contact layers being arranged to permit selective addressing in said array.
15. A method of manufacture of an electroluminescent device according to claim 1 comprising providing a layer of a light emissive polymer between first and second contact layers, wherein the first contact layer is selected so that an application of an electric field to said device charge carriers of a first type are injected into the light emissive layer, characterised by the steps of:
 - a) depositing onto a substrate one of said first and second contact layers;
 - b) depositing on said contact layer a layer of a precursor polymer as a polymer film and then heating the deposited precursor polymer to a high temperature to form the light emissive layer as a semiconductive conjugated polymer; and
 - c) providing the other one of said first and second contact layers, the second contact layer being selected and arranged so that on application of an electric field to said device charge carriers of a second type are injected into the light emissive layer, wherein the semiconductive conjugated polymer has a sufficiently low concentration of extrinsic charge carriers that on applying an electric field between the first and second contact layers across a semiconductor layer so as to render the second contact layer positive relative to the first contact layer charge carriers of said first and second types are injected into the semiconductor layer and combine to form in the conjugated polymer charge carrier pairs which decay radiatively so that radiation is emitted from the conjugated polymer.
16. A method as claimed in claim 15, comprising the steps of firstly depositing the first charge injecting contact layer onto the substrate to form a composite substrate before the step of depositing the precursor polymer

as a thin dense polymer film onto the first charge injecting contact layer.

17. A method as claimed in either of claims 15 or 16, wherein the precursor polymer is soluble and is deposited as a thin polymer film on the substrate by spin-coating.
- 5 18. A method as claimed in any of claims 15 to 17, wherein the precursor polymer is a precursor polymer for poly (p-phenylenevinylene) [PPV].
- 10 19. A method as claimed in any of claims 15 to 18, wherein the thin dense polymer film is of uniform thickness in the range 10nm to 5µm.
- 20 20. A method as claimed in any of claims 15 to 19, wherein the first charge injecting contact layer is a thin layer of aluminium one surface having formed a thin oxide layer, the thin oxide layer of the first charge injecting contact layer being placed in contact with the semiconductor layer.
- 15 21. A method as claimed in any of claims 15 to 20, wherein the second charge injecting contact layer is selected from the group comprising aluminium and gold.
22. A method as claimed in any of claims 16 to 19, wherein the first contact layer is selected from the group comprising aluminium and magnesium/silver alloy and the second contact layer is indium oxide.
- 20 23. A method as claimed in any of claims 15 to 19 wherein the first contact layer comprises amorphous silicon and the second contact layer is selected from the group comprising aluminium, gold and indium oxide.
24. A method as claimed in any of claims 15 to 23, wherein the first and second charge injecting contact layers are deposited by evaporation.
- 25 25. A method as claimed in any of claims 15 to 23, wherein the supporting substrate is silica glass.
26. A method as claimed in any of claims 15 to 24 wherein the supporting substrate is a flexible transparent polymer.
- 30

Patentansprüche

1. Eine elektrolumineszierende Anordnung, die aufweist:
35 eine lichtemittierende Schicht (4) in der Form eines dünnen, dichten Polymerfilms, der mindestens ein Polymer aufweist;
eine erste Kontaktschicht (2), die auf einer Seite der lichtemittierenden Schicht angeordnet ist, die so ausgewählt ist, daß bei Anlegen eines elektrischen Feldes an diese Anordnung Ladungsträger einer ersten Art in die lichtemittierende Schicht injiziert werden; und
40 eine zweite Kontaktschicht (5), die auf der anderen Seite der lichtemittierenden Schicht angeordnet ist, gekennzeichnet dadurch, daß die zweite Kontaktschicht so ausgewählt ist, daß bei Anlegen eines elektrischen Feldes an diese Anordnung Ladungsträger einer zweiten Art in die lichtemittierende Schicht injiziert werden; und
45 die lichtemittierende Schicht ein halbleitendes konjugiertes Polymer aufweist, welches in einer Volumenfraktion Vorhanden ist, die das Erreichen der Durchsickerungsschwelle für Ladungstransport des Polymerfilms ermöglicht, wobei dieses halbleitende konjugierte Polymer eine ausreichend niedrige Konzentration von extrinsischen Ladungsträgern hat, daß bei Anlegen eines elektrischen Feldes zwischen der ersten und zweiten Kontaktschicht über die lichtemittierende Schicht, um so die zweite Kontaktschicht gegenüber der ersten Kontaktschicht positiv zu machen, Ladungsträger der ersten und zweiten Art in die lichtemittierende Schicht injiziert werden und kombinieren, um Ladungsträgerpaare in dem halbleitenden konjugierten Polymer zu bilden, wobei diese Paare strahlend zerfallen, so daß Strahlung von diesem konjugierten Polymer emittiert wird.
- 50
2. Eine elektrolumineszierende Anordnung nach Anspruch 1, worin das konjugierte Polymer in Poly(p-Phenylenvinyl) [PPV] der Formel
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ist, worin der Phenylring wahlweise einen oder mehrere Substituenten trägt, wobei jeder unabhängig aus Alkyl (bevorzugt Methyl), Alkyloxy (bevorzugt Methoxy oder Ethoxy), Halogen (bevorzugt Chlor oder Brom) oder Nitro ausgewählt ist.

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3. Eine elektrolumineszierende Anordnung nach einem der Ansprüche 1 oder 2, worin der dünne, dichte Polymerfilm im wesentlichen gleichmäßig dick im Bereich von 10 nm bis 5 µm ist.

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4. Eine elektrolumineszierende Anordnung nach einem der vorangehenden Ansprüche, worin das konjugierte Polymer einen Halbleiter-Bandabstand im Bereich von 1 eV bis 3,5 eV hat.

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5. Eine elektrolumineszierende Anordnung nach einem der vorangehenden Ansprüche, worin die erste ladungsinjizierende Kontaktschicht eine dünne Schicht aus Aluminium (2) ist, eine Fläche eine dünne Oxidschicht (3) gebildet hat, die erste Fläche der Halbleiterschicht (4) im Kontakt mit dieser Oxidschicht ist.

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7. Elektrolumineszierende Anordnung nach Anspruch 5, worin die zweite ladungsinjizierende Kontaktschicht (5) aus der Gruppe, die Aluminium und Gold enthält, ausgewählt ist.

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9. Elektrolumineszierende Anordnung nach Anspruch 6, worin die zweite Kontaktschicht (5) Indiumoxid oder Indiumzinnoxid aufweist.

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10. Elektrolumineszierende Anordnung nach einem der Ansprüche 1 bis 4, worin die erste Kontaktschicht amorphes Silizium aufweist und die zweite Kontaktschicht aus der Gruppe, die Aluminium, Gold und Indiumoxid enthält, ausgewählt ist.

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12. Elektrolumineszierende Anordnung nach Anspruch 11, worin das Trägersubstrat Silikatglas ist.

13. Elektrolumineszierende Anordnung nach Anspruch 11 oder 12, worin das Trägersubstrat ein flexibles durchlässiges, d.h. transparentes Polymer ist.

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14. Eine Reihe von elektrolumineszierenden Anordnungen, jede elektrolumineszierende Anordnung nach einem der Vorangehenden Ansprüche, wobei die ersten und die zweiten ladungsinjizierenden Kontaktschichten angeordnet sind, um eine selektive Adressierung in dieser Reihe zu gestatten.

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15. Verfahren zur Herstellung von einer elektrolumineszierenden Anordnung nach Anspruch 1, das umfaßt, die eine Schicht eines lichtemittierenden Polymers zwischen der ersten und der zweiten Kontaktschicht vorzusehen, wobei die erste Kontaktschicht so ausgewählt ist, daß ein Anlegen eines elektrischen Feldes an diese Anordnung Ladungsträger einer ersten Art in die lichtemittierende Schicht injiziert, gekennzeichnet durch die Schritte:

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- a) Auftragung der einen der ersten und zweiten Kontaktschicht auf ein Substrat;
- b) Auftragung einer Schicht von Vorläufer-Polymer als ein Polymerfilm auf der Kontaktschicht und dann Erhitzung des abgelagerten Vorläufer-Polymers auf eine hohe Temperatur, um die lichtemittierende Schicht als ein halbleitendes konjugiertes Polymer zu bilden; und
- c) Bereitstellung der anderen der ersten und zweiten Kontaktschicht, wobei die zweite Kontaktschicht

ausgewählt und so angeordnet wird, daß bei Anlegen eines elektrischen Feldes an die Anordnung Ladungsträger einer zweiten Art in die lichtemittierende Schicht injiziert werden, wobei das halbleitende konjugierte Polymer eine ausreichend niedrige Konzentration von extrinsischen Ladungsträgern hat, daß bei Anlegen eines elektrischen Feldes zwischen der ersten und zweiten Kontaktschicht über eine halbleitende Schicht, um so die zweite Kontaktschicht positiv gegenüber der ersten Kontaktschicht zu machen, Ladungsträger der ersten und zweiten Art in die halbleitende Schicht injiziert werden und kombinieren, um Ladungsträgerpaare in dem konjugierten Polymer zu bilden, wobei diese Paare strahlend zerfallen, so daß Strahlung von diesem konjugierten Polymer emittiert wird.

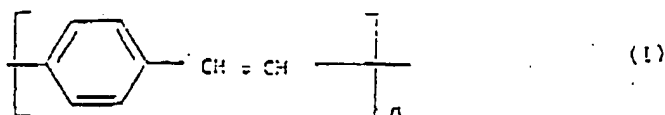
- 10 16. Verfahren nach Anspruch 15, das die Schritte aufweist, zuerst die erste ladungsinjizierende Kontaktschicht auf das Substrat abzulagern, um ein zusammengesetztes Substrat zu bilden, vor dem Schritt der Auftragung des Vorläufer-Polymers als dünnen, dichten Polymerfilm auf die erste ladungsinjizierende Kontaktschicht.
- 15 17. Verfahren nach Anspruch 15 oder 16, wobei das Vorläufer-Polymer löslich ist und als ein dünner Polymerfilm auf dem Substrat durch Schleuderbeschichtung abgelagert ist.
18. Verfahren nach einem der Ansprüche 15 bis 17, wobei das Vorläufer-Polymer ein Vorläufer-Polymer für Poly(p-Phenylenvinyl) [PPV] ist.
- 20 19. Verfahren nach einem der Ansprüche 15 bis 18, wobei der dünne, dichte Polymerfilm von gleichmäßiger Dicke im Bereich von 10nm bis 5 µm ist.
20. Verfahren nach einem der Ansprüche 15 bis 19, wobei die erste ladungsinjizierende Kontaktschicht eine dünne Schicht aus Aluminium ist, eine Fläche eine dünne Oxidschicht gebildet hat, die dünne Oxidschicht der ersten ladungsinjizierenden Kontaktschicht im Kontakt mit der halbleitenden Schicht plaziert ist.
- 25 21. Verfahren nach einem der Ansprüche 15 bis 20, wobei die zweite ladungsinjizierende Kontaktschicht aus der Gruppe, die Aluminium und Gold enthält, ausgewählt ist.
- 30 22. Verfahren nach einem der Ansprüche 16 bis 19, wobei die erste Kontaktschicht aus der Gruppe, die Aluminium und Magnesium/Silber Legierungen enthält, ausgewählt ist, und die zweite Kontaktschicht Indiumoxid ist.
23. Verfahren nach einem der Ansprüche 15 bis 19, wobei die erste Kontaktschicht amorphes Silizium aufweist und die zweite Kontaktschicht aus der Gruppe, die Aluminium, Gold und Indiumoxid enthält, ausgewählt ist.
- 35 24. Verfahren nach einem der Ansprüche 15 bis 23, wobei die erste und zweite ladungsinjizierende Kontaktschicht durch Evaporation abgelagert bzw. abgeschieden werden.
- 40 25. Verfahren nach einem der Ansprüche 15 bis 23, wobei das Trägersubstrat Silikatglas ist.
26. Verfahren nach einem der Ansprüche 15 bis 24, wobei das Trägersubstrat ein flexibles, transparentes Polymer ist.

Revendications

1. Dispositif électroluminescent comprenant :
 - 50 une couche d'émission de lumière (4) sous forme d'un film polymérique dense mince comprenant au moins un polymère ;
 - une première couche de contact (2) placée sur une face de la couche d'émission de lumière, choisie de telle sorte que, par application d'un champ électrique audit dispositif, des porteurs de charges d'un premier type soient injectés dans la couche d'émission de lumière ; et
 - 55 une seconde couche de contact (5) placée sur l'autre face de la couche d'émission de lumière, caractérisée en ce que la seconde couche de contact est choisie de telle sorte qu', par application d'un champ électrique audit dispositif, des porteurs de charges d'un second type soient injectés dans la couche d'émission de lumière ; et

la couche d'émission de lumière comprenant un polymère conjugué semiconducteur présent en une fraction volumique qui permet d'atteindre le seuil de percolation pour le transport de charges du film polymérique, ledit polymère conjugué semiconducteur ayant une concentration suffisamment faible de porteurs de charges extrinsèques pour que, par application d'un champ électrique entre les première et seconde couches de contact de part et d'autre de la couche d'émission de lumière de manière à rendre la seconde couche de contact positive par rapport à la première couche de contact, des porteurs de charges desdits premier et second types soient injectés dans la couche d'émission de lumière et s'associent en formant des paires de porteurs de charges dans le polymère conjugué semiconducteur, paires qui présentent une extinction par rayonnement de telle sorte qu'un rayonnement soit émis par ledit polymère conjugué.

2. Dispositif électroluminescent suivant la revendication 1, dans lequel le polymère conjugué est un poly(p-phénylènevinylène) [PPV] de formule



dans laquelle le noyau phénylène peut porter facultativement un ou plusieurs substituants choisis chacun indépendamment entre des substituants alkyle (de préférence méthyle), alkoxy (de préférence méthoxy ou éthoxy), halogéno (de préférence chloro ou bromo) et nitro.

3. Dispositif électroluminescent suivant l'une des revendications 1 et 2, dans lequel le film polymérique dense mince possède une épaisseur pratiquement uniforme comprise dans l'intervalle de 10 nm à 5 µm.
4. Dispositif électroluminescent suivant l'une quelconque des revendications précédentes, dans lequel le polymère conjugué possède une largeur de bande semiconductrice comprise dans l'intervalle de 1 eV à 3,5 eV.
5. Dispositif électroluminescent suivant l'une quelconque des revendications précédentes, dans lequel la première couche de contact d'injection de charges est une couche mince d'aluminium (2) dont une surface a formé une couche mince d'oxyde (3), la première surface de la couche semiconductrice (4) étant en contact avec ladite couche d'oxyde.
6. Dispositif électroluminescent suivant l'une quelconque des revendications 1 à 4, dans lequel la première couche de contact est choisie dans le groupe comprenant l'aluminium ou un alliage de magnésium et d'argent.
7. Dispositif électroluminescent suivant la revendication 5, dans lequel la seconde couche de contact d'injection, de charges (5) est choisie dans le groupe comprenant l'aluminium et l'or.
8. Dispositif électroluminescent suivant l'une quelconque des revendications précédentes, dans lequel au moins une des première et seconde couches de contact d'injection de charges est au moins semi-transparente.
9. Dispositif électroluminescent suivant la revendication 6, dans lequel la seconde couche de contact (5) comprend de l'oxyde d'indium ou de l'oxyde d'indium-étain.
10. Dispositif électroluminescent suivant l'une quelconque des revendications 1 à 4, dans lequel la première couche de contact comprend du silicium amorphe et la seconde couche de contact est choisie dans le groupe comprenant l'aluminium, l'or et l'oxyde d'indium.
11. Dispositif électroluminescent suivant l'une quelconque des revendications précédentes, dans lequel au moins une des première et seconde couches de contact d'injection de charges est également en contact avec un substrat servant de support.
12. Dispositif électroluminescent suivant la revendication 11, dans lequel le substrat de support est constitué

d'un verre de silic .

13. Dispositif électroluminescent suivant la revendication 11 ou 12, dans lequel le substrat de support est constitué d'un polymère transparent flexible.
- 5 14. Réseau de dispositifs électroluminescents, chaque dispositif électroluminescent étant un dispositif suivant l'une quelconque des revendications précédentes, lesdites première et seconde couches de contact d'injection de charges étant disposées de manière à permettre l'adressage sélectif dudit réseau.
- 10 15. Procédé de production d'un dispositif électroluminescent suivant la revendication 1, comprenant la formation d'une couche d'un polymère d'émission de lumière entre des première et seconde couches de contact, dans lequel la première couche de contact est choisie de telle sorte que, par application d'un champ électrique audit dispositif, des porteurs de charges d'un premier type soient injectés dans la couche d'émission de lumière, caractérisé par les étapes consistant :
 - 15 a) à déposer sur un substrat une desdites première et seconde couches de contact ;
 - b) à déposer sur ladite couche de contact une couche d'un polymère précurseur sous forme d'un film polymérique, puis à chauffer le polymère précurseur déposé à une température élevée pour former la couche d'émission de lumière constituée d'un polymère conjugué semiconducteur ; et
 - 20 c) à former l'autre desdites première et seconde couches de contact, la seconde couche de contact étant choisie et disposée de telle sorte que, par application d'un champ électrique audit dispositif, des porteurs de charges d'un second type soient injectés dans la couche d'émission de lumière, le polymère conjugué semiconducteur ayant une concentration suffisamment faible de porteurs de charges extrinsèques pour que, par application d'un champ électrique entre les première et seconde couches de contact de part et d'autre d'une couche semiconductrice de manière à rendre la seconde couche de contact positive par rapport à la première couche de contact, des supports de charges desdits premier et second types soient injectés dans la couche semiconductrice et s'associent en formant dans le polymère conjugué des paires de porteurs de charges qui présentent une extinction par rayonnement de telle sorte qu'un rayonnement soit émis par le polymère conjugué.
- 30 16. Procédé suivant la revendication 15, comprenant les étapes consistant à déposer tout d'abord la première couche de contact d'injection de charges sur le substrat pour former un substrat composite avant l'étape de dépôt du polymère précurseur sous forme d'un film polymérique dense mince sur la première couche de contact d'injection de charges.
- 35 17. Procédé suivant l'une des revendications 15 et 16, dans lequel le polymère précurseur est soluble et est déposé sous forme d'un film polymérique mince sur le substrat par revêtement centrifuge.
18. Procédé suivant l'une quelconque des revendications 15 à 17, dans lequel le polymère précurseur est un polymère précurseur pour le poly(p-phénylènevinylène) [PPV].
- 40 19. Procédé suivant l'une quelconque des revendications 15 à 18, dans lequel le film polymérique dense mince possède une épaisseur uniforme comprise dans l'intervalle de 10 nm à 5 µm.
20. Procédé suivant l'une quelconque des revendications 15 à 19, dans lequel la première couche de contact d'injection de charges est une couche mince d'aluminium sur une surface de laquelle a été formée une couche d'oxyde mince, la couche d'oxyde mince de la première couche de contact d'injection de charges étant placée en contact avec la couche semiconductrice.
- 45 21. Procédé suivant l'une quelconque des revendications 15 à 20, dans lequel la seconde couche de contact d'injection de charges est choisie dans le groupe comprenant l'aluminium et l'or.
- 50 22. Procédé suivant l'une quelconque des revendications 16 à 19, dans lequel la première couche de contact est choisie dans le groupe comprenant l'aluminium et un alliage magnésium/argent, et la seconde couche de contact est constituée d'oxyde d'indium.
- 55 23. Procédé suivant l'une quelconque des revendications 15 à 19, dans lequel la première couche de contact comprend du silicium amorphe et la seconde couche de contact est choisie dans le groupe comprenant l'aluminium, l'or et l'oxyde d'indium.
24. Procédé suivant l'une quelconque des revendications 15 à 23, dans lequel les première et seconde cou-

ches de contact d'injection des charges sont déposées par évaporation.

25. Procédé suivant l'une quelconque des revendications 15 à 23, dans lequel le substrat de support est constitué de verre de silice.

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26. Procédé suivant l'une quelconque des revendications 15 à 24, dans lequel le substrat de support est constitué d'un polymère transparent flexible.

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FIG. 1

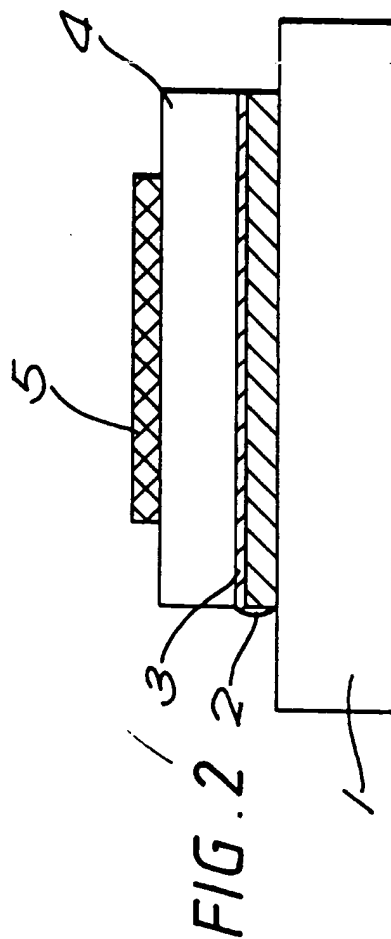
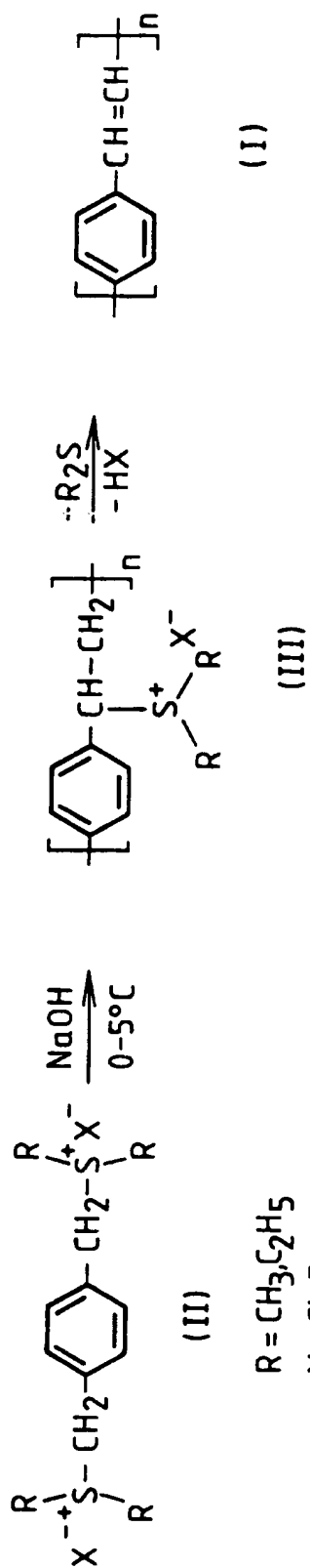


FIG. 3

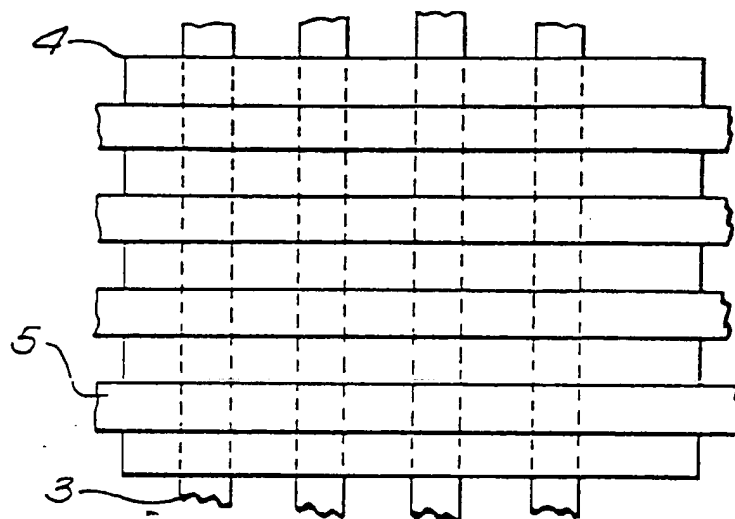


FIG. 4

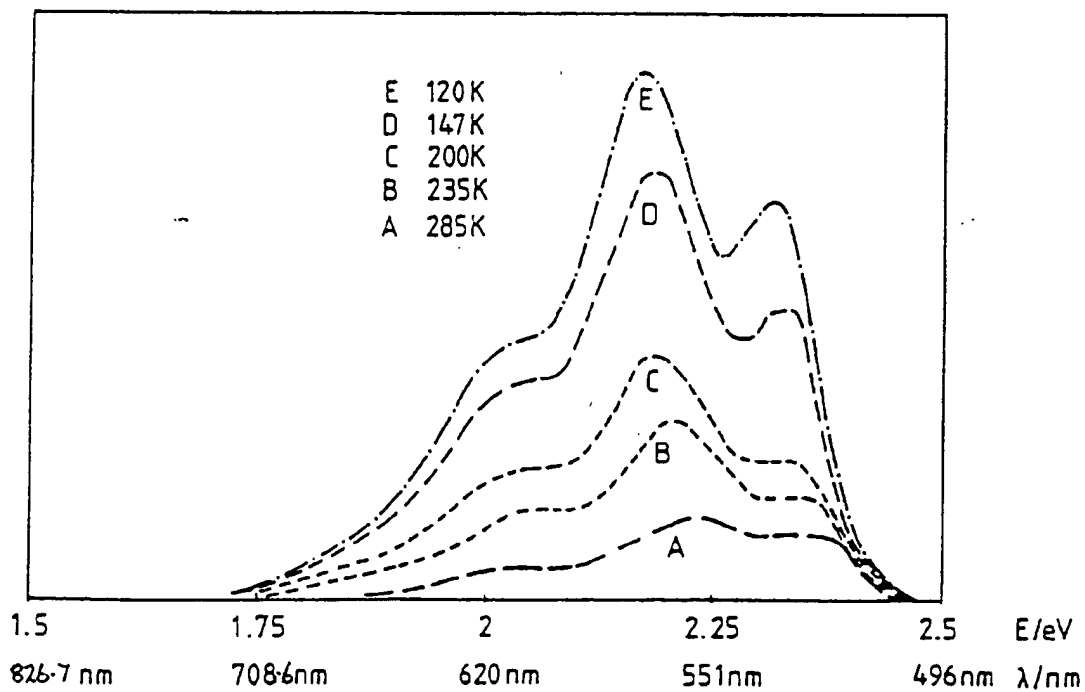


FIG. 5

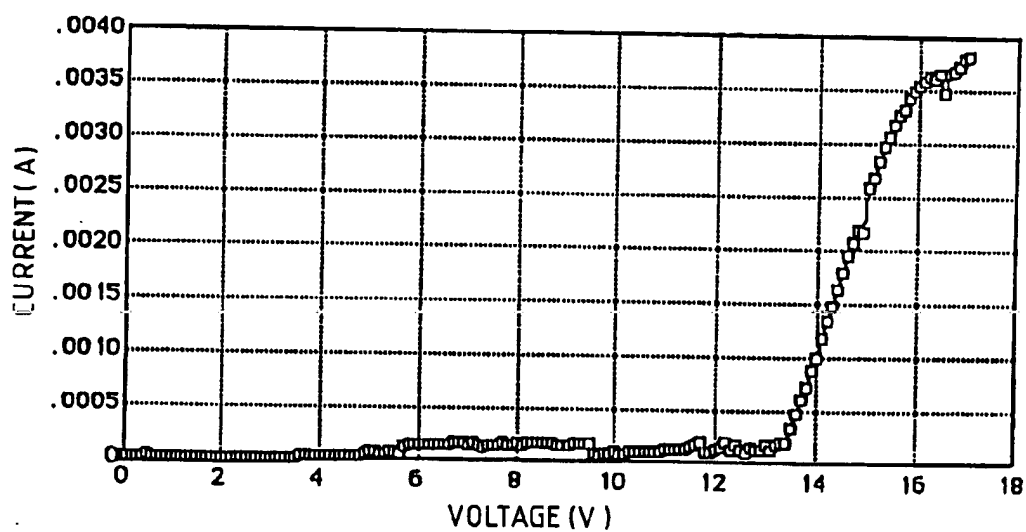


FIG. 6

